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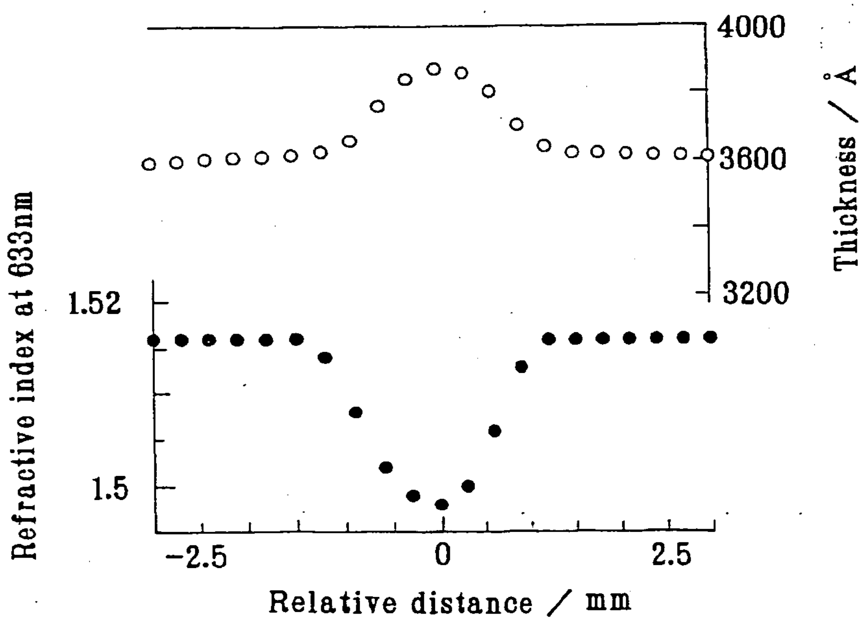
(54) **Glass material variable in volume by irridation with ultraviolet light**

(57) A glass material variable in volume by irradiation with ultraviolet light has a GeO_2-SiO_2 glass composition having a GeO_2 content of 0.5 to 90 mol %, and is in the form of a thin film formed in an argon atmosphere or in an argon-oxygen mixed gas atmosphere by the high-frequency sputtering method.

Fig.1



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Description

The present invention relates to a glass material variable in volume by irradiation with ultraviolet light (hereinafter often referred to as a "variable-volume glass material").

A silica glass capable of transmitting light in the ultraviolet to near infrared range is used as the matrix of an optical communication fiber, the core portion of which is usually doped with GeO_2. It has been found out that this optical fiber is increased by about 1 x 10^{-4} in the refractive index of the core thereof when irradiated with an argon ion laser beam of 488 nm in wavelength or an excimer laser beam of 248 nm in wavelength (K. O. Hill et al., Applied Physics Letters, Vol. 32, No. 10, 1978, P. P. 647 ~ 649, and R. M. Atkins et.al., Electronics Letters, 1993, Vol. 29, No. 4, P.P. 385 ~ 387). It has been reported that the mechanism of refractive index change is sequential occurrence of two processes: (1) that structural defects are induced in the glass by light to bring about strong absorption in the ultraviolet range, and (2) that the density of the glass is increased, i.e., the volume thereof is decreased due to formation of the structural defects.

A refractive index change is also recognized in a GeO_2-SiO_2 glass produced by the sol-gel method (K. D. Simnon et al., Optics Letter, 1993, Vol. 18, No. 1, P.P. 25 ~ 27). In this case, however, the amount of refractive index change is no more than about $3x10^{-5}$.

In both the foregoing cases, therefore, a difficulty is encountered in applying the glass to a hologram and the like in which cases a level of 10^{-2} is required as the amount of refractive index change.

Further, ion exchange, crystallization, etc. have been proposed as means for realizing an increase in the volume of glass by irradiation thereof with light. However, there are no reports of a glass wherein volume expansion thereof can be induced by irradiation thereof with light at room temperature while keeping it in an amorphous state.

Accordingly, a principal object of the present invention is to provide a glass material wherein volume expansion thereof by a level of 10^{-2} can be induced by irradiation thereof with ultraviolet light at room temperature while keeping it in an amorphous state.

As a result of intensive investigations made having regard to the foregoing status of the prior art, the inventors of the present invention have found out that the foregoing object can be attained when a glass having a specific composition is used to form a thin glass film in a specific gas atmosphere controlled in oxygen content by the high-frequency sputtering method.

Specifically, the present invention provides a glass material wherein a volume change thereof by a level of 10^{-2} can be induced by irradiation thereof with ultraviolet light, and particularly a glass material variable in volume by irradiation with ultraviolet light which material has a GeO_2-SiO_2 glass composition having a GeO_2 content of 0.5 to 90 mol %, and is in the form of a thin film formed in an argon atmosphere or in an argon-oxygen mixed gas atmosphere having an oxygen content of at most 20 vol. % by the high-frequency sputtering method.

In a thin GeO_2-SiO_2 glass film formed under specific conditions by the high-frequency sputtering method according to the present invention, an increase by a level of 10^{-2} in the volume thereof can be induced by irradiation thereof with an ultraviolet laser beam at room temperature while keeping it in an amorphous state. Accordingly, it is applicable to an optical memory, a hologram recording medium, etc.

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawing, in which;

Fig. 1 is a two-dimensional diagram showing a change in the refractive index of the glass material of the present invention and a change in the thickness thereof after the glass material is irradiated with ultraviolet radiation.

The optical induction variable-volume glass material made of GeO_2-SiO_2 glass according to the present invention is obtained in the form of a thin film on a substrate such as a single silicon crystal by the high-frequency sputtering method. GeO_2-SiO_2 glass is especially useful since it is high in transparency in the visible light range and excellent in chemical durability and mechanical durability.

A GeO_2-SiO_2 glass having a Ge_2O content of 0.5 to 90 mol %, preferably 3 to 60 mol %, is especially suitably used as such glass. When the GeO_2 content is too low, the GeO_2-SiO_2 glass cannot secure a large volume change when irradiated with light. On the other hand, when it is too high, the glass is sometimes colored yellow or lowered in water resistance.

High-frequency sputtering can be effected in an argon or argon-oxygen mixed gas atmosphere (oxygen content: at most 20 vol. %, preferably at most 10 vol. %) according to a customary method though conditions thereof are not particularly limited. When the oxygen content of the argon-oxygen mixed gas atmosphere exceeds 20 vol. %, a thin film having the desired feature of being variable in volume by irradiation thereof with ultraviolet light cannot be obtained. The thickness of the thin glass film is usually about 0.1 to 10 μm (100 to 100,000 Å).

The thin film thus obtained may be heat-treated in vacuo or in an inert gas such as argon or nitrogen at 200 to 800 °C, preferably 300 to 650 °C, for the purpose of adjusting the volume change thereof and improving the laser beam resistance, etc. thereof.

The light usable for inducing volume expansion of the thin film is preferably an ultraviolet light of at most 400 nm in wavelength. A more specific preferable light source is a pulse laser of at least 1 mJ/cm^2 in energy density, examples of which include an argon-fluorine (ArF) excimer laser of 193 nm in wavelength, a krypton-fluorine (KrF) excimer laser of 248 nm in wavelength, a

xenon-chlorine (XeCl) excimer laser of 308 nm in wavelength, a xenon-fluorine (XeF) excimer laser of 350 nm in wavelength, and yttrium-aluminum-garnet (YAG) lasers respectively emitting third harmonics (355 nm) and fourth harmonics (266 nm).

The features of the present invention will now be made clearer while showing Examples and Comparative Examples.

Example 1:

A thin glass film of 33 mol % GeO_2-67 mol % SiO_2 was deposited on a single silicon crystal substrate at a rate of about 8 nm/min over about 15 minutes under conditions involving a gas atmosphere composition of 100% argon (Ar), a gas flow rate of 3 cc/mm and a pressure of about 10^{-2} Torr in a chamber. Desired adjustment of the composition of the thin film was confirmed by XPS (X-ray photoelectron spectroscopy).

Further, a thin film of about 6 μm in thickness was formed on a SiO_2 glass substrate according to substantially the same procedure as described above, and then examined by X-ray diffractometry to observe no sharp diffraction peaks assigned to GeO_2 or SiO_2.

The thin glass film thus obtained was heat-treated in vacuo at 500 °C for 1 hour, and then irradiated with 1,200 ArF excimer laser beam pulses of 248 nm in wavelength and 10 mJ/cm^2 in power density. Thereafter, the refractive index of it was examined with an ellipsometer using an He-Ne laser of 633 nm in wavelength as the light source. The results are shown in Fig. 1.

As is apparent from Fig. 1, it was confirmed that the thin film was increased by about 8% in thickness, i.e., volume, in the region thereof irradiated with the laser beam to be thereby decreased by about 1.2% in refractive index.

Example 2:

A thin glass film of 50 mol % GeO_2 -50 mol % SiO_2 formed in substantially the same manner as in Example 1 was heat-treated in an argon atmosphere at 500 °C for 1 hour, and then irradiated with the same excimer laser beam pulses as in Example 1. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source. As a result, it was confirmed that the thin film was increased by about 10% in thickness in the region thereof irradiated with the laser beam to be thereby decreased by about 1.5% in refractive index.

Example 3:

A thin film formed using a glass having a 5 mol % GeO_2-95 mol % SiO_2 glass composition in substantially the same manner as in Example 1 was heat-treated in vacuo at 500 °C for 1 hour, and then irradiated with 1,400 ArF excimer laser beam pulses in substantially the same manner as in Example 1. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source. As a result, it was confirmed that the thin film was increased by 1% in thickness in the region thereof irradiated with the laser beam to be thereby decreased by 0.15% in refractive index.

Example 4:

A thin film formed using a glass having a 55 mol % GeO_2-45 mol % SiO_2 glass composition in substantially the same manner as in Example 1 was heat-treated in vacuo at 500 °C for 1 hour, and then irradiated with 1,100 XeCl excimer laser beam pulses in substantially the same manner as in Example 1. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source. As a result, it was confirmed that the thin film was increased by 6% in thickness in the region thereof irradiated with the laser beam to be thereby decreased by 0.9% in refractive index.

Example 5:

A thin film formed using a glass having a 20 mol % GeO_2-80 mol % SiO_2 glass composition in substantially the same manner as in Example 1 was heat-treated in vacuo at 500 °C for 1 hour, and then irradiated with 1,400 KrF excimer laser beam pulses in substantially the same manner as in Example 1. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source. As a result, it was confirmed that the thin film was increased by 5% in thickness in the region thereof irradiated with the laser beam to be thereby decreased by 0.75% in refractive index.

Example 6:

A thin film formed using a glass having a 55 mol % GeO_2-45 mol % SiO_2 glass composition in substantially the same manner as in Example 1 was heat-treated in vacuo at 500 °C for 1 hour, and then irradiated with 1,100 YAG laser beam pulses of 266 nm in wavelength in substantially the same manner as in Example 1. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source. As a result, it was confirmed that the thin film was increased by 4% in thickness in the region thereof irradiated with the laser beam to be thereby decreased by 0.6% in refractive index.

Comparative Example 1:

A thin SiO_2 glass film was deposited on a single silicon crystal substrate at a rate of about 8 nm/min over about 15 minutes under conditions involving a gas at-

mosphere composition of 100% argon (Ar), a gas flow rate of 3 cc/min and a pressure of about 10^{-2} Torr in a chamber.

The thin glass film thus obtained was irradiated with 6,000 ArF excimer laser beam pulses of 248 nm in wavelength and 10 mJ/cm^2 in power density. Thereafter, the refractive index of it was examined with the ellipsometer using the He-Ne laser of 633 nm in wavelength as the light source to recognize no change in the refractive index thereof.

Comparative Example 2:

A 33 mol % GeO_2-67 mol % SiO_2 glass was deposited on a silicon substrate under substantially the same conditions as in Comparative Example 1, and then irradiated with ArF excimer laser beam pulses of 248 nm in wavelength and 10 mJ/cm^2 in power density, whereby the surface of the thin film was thermally damaged to make it impossible to evaluate the refractive index thereof with the ellipsometer.

Comparative Example 3:

Sputtering of a 20 mol % GeO_2 -80% mol SiO_2 glass on a single silicon crystal substrate was attempted under conditions involving a gas atmosphere composition of 35% O_2-65% argon (Ar), a gas flow rate of 3 cc/min and a pressure of about 10^{-2} Torr in a chamber. The deposition rate was very slow. Moreover, no substantial change in the refractive index of the resulting thin glass film by irradiation thereof with light was recognized.

It will be apparent that a wide variety of different embodiments are possible without any departure from the spirit and ambit of the present invention. Accordingly, the present invention is not restricted to the specific embodiments thereof except for the limitations as specified in the appended claims.

The aforegoing description has been given by way of example only and it will be appreciated by a person skilled in the art that modifications can be made without departing from the scope of the present invention.

Claims

1. A glass material variable in volume by irradiation thereof with ultraviolet light, which has a GeO_2-SiO_2 glass composition having a GeO_2 content of 0.5 to 90 mol %, and is in the form of a thin film formed in an argon atmosphere or in an argon-oxygen mixed gas atmosphere having an oxygen content of at most 20 vol. % by a high-frequency sputtering method.

2. A glass material as claimed in claim 1, wherein said GeO_2 content is 3 to 60 mol %.

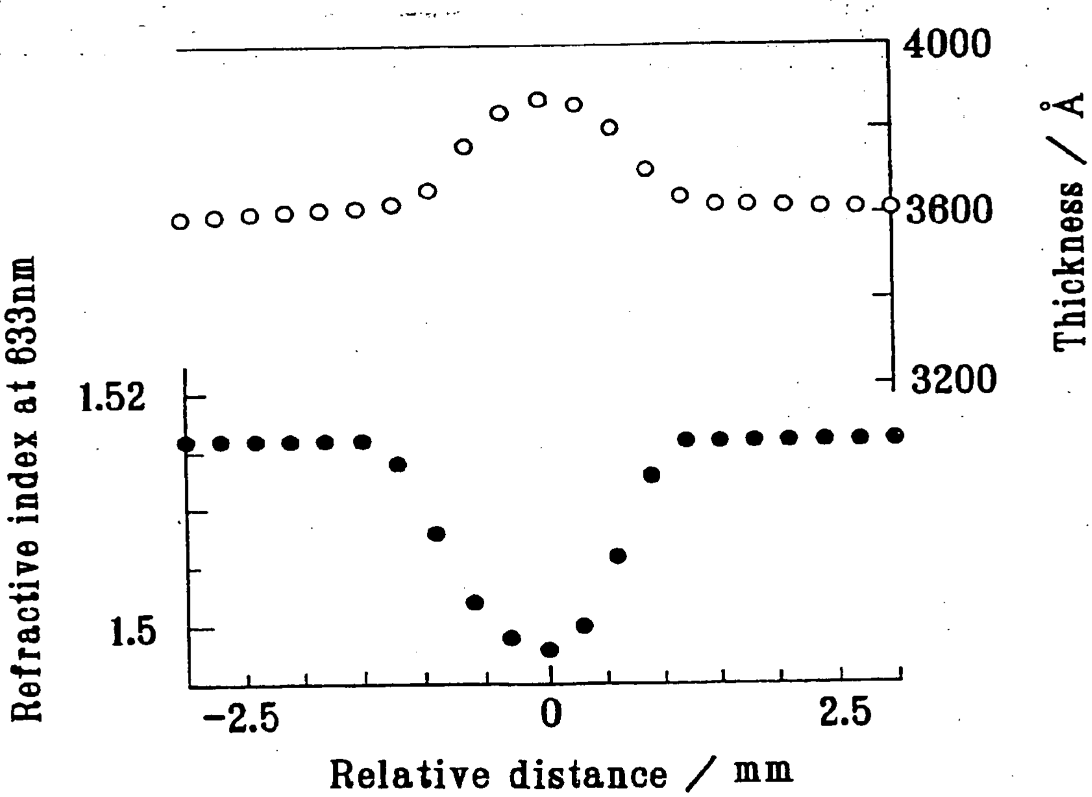
3. A glass material as claimed in claim 1, wherein said thin film as an intermediate material is heat-treated in vacuo at 200 to 800 °C before the volume change thereof is induced by irradiation with ultraviolet light.

4. A glass material as claimed in claim 3, wherein the heat treatment temperature is 300 to 650 °C.

5. A glass material as claimed in claim 1 or 3, wherein the volume change of said thin film as an intermediate material is induced by irradiation thereof with an ultraviolet light of at most 400 nm in wavelength.

6. A method of forming a glass material variable in volume by irradiation thereof with ultraviolet light, comprising forming a thin film of a GeO_2-SiO_2 glass composition having a GeO_2 content of 0.5 to 90 mol % a high-frequency sputtering method in an argon atmosphere or in an argon-oxygen atmosphere having an oxygen content of at most 20 vol %.

Fig.1


4000
3600
3200
Thickness / Å
1.52
1.5
Refractive index at 633nm
-2.5
0
2.5
Relative distance / mm

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 8588

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	APPLIED PHYSICS LETTERS, 17 JAN. 1994, USA, vol. 64, no. 3, ISSN 0003-6951, pages 282-284, XP002026432 NISHII J ET AL: "Characteristics of 5-eV absorption band in sputter deposited GeO/sub 2/-SiO/sub 2/ thin glass films" * page 282, right-hand column, paragraph 3 * * page 283, left-hand column, last paragraph * * page 284, right-hand column * ---	1-6	C03C3/076 C03C17/02 C03C4/04 C03B19/14 C23C14/10 G02B6/12
P,X	APPLIED PHYSICS LETTERS, 1 APRIL 1996, AIP, USA, vol. 68, no. 14, ISSN 0003-6951, pages 2011-2013, XP000585126 SIMMONS-POTTER K ET AL: "Novel process for the production of large, stable photosensitivity in glass films" * page 2011 * ---	1-6	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
P,X	OPTICS LETTERS, 1 SEPT. 1996, OPT. SOC. AMERICA, USA, vol. 21, no. 17, ISSN 0146-9592, pages 1360-1362, XP000627761 NISHII J ET AL: "Preparation of Bragg gratings in sputter-deposited GeO/sub 2/-SiO/sub 2/ glasses by excimer-laser irradiation" * page 1360, left-hand column - right-hand column, paragraph 1 * -----	1-6	C03C C03B C23C G02B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 February 1997	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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